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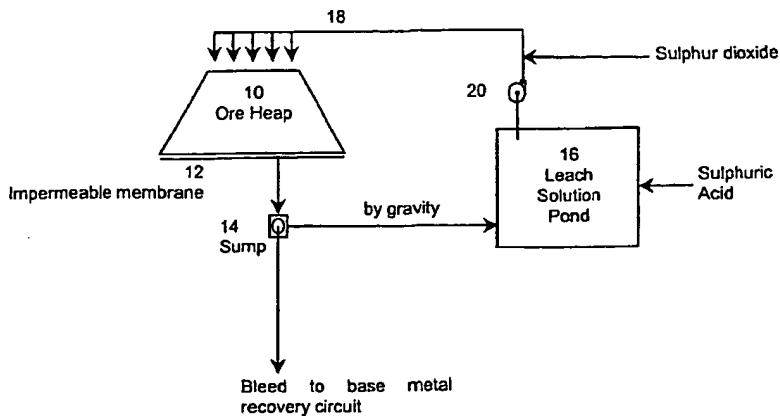
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: HEAP LEACHING BASE METALS FROM OXIDE ORES



- (57) Abstract: In accordance with the present invention there is provided a method for the heap leaching of base metals from oxide ores, the method characterised by the method steps of: a) Establishing at least one heap of the oxide ore containing the base metals to be leached; b) Irrigating at least one of the or each heaps with a leach solution containing both sulphuric acid and dissolved sulphur dioxide; and c) Providing at least one leach solution pond or other suitable container to which pregnant leach solution recovered at or near a base of the or each heap may be fed.

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"Heap Leaching Base Metals from Oxide Ores"**Field of the Invention**

The present invention relates to the heap leaching of base metals from oxide ores. More particularly, the present invention is particularly intended for
5 application in the recovery of nickel and cobalt from lateritic ores.

Background Art

The application of heap leaching techniques in the recovery of base metals, for example copper, from oxide ore deposits is well established. For example, if copper is the base metal of interest and the host rock is sufficiently oxidised, the
10 oxide ore can be crushed to a suitable size, stacked in heaps and leached with a sulphuric acid solution (SME Minerals Processing Handbook, Ed. NL Weiss, Society of Mineral Engineers ISBN 0-89520-433-6).

It is often the case that the ore, after crushing, will contain a significant level of fine particulate material, such as clay or clay-like material. This material, if
15 preventative steps are not taken, can interfere with the permeability of the heap, and consequently reduce the efficiency of the heap leach process. In dealing with such ores, it is common practice to agglomerate the ore with water or process solution, and with cement. The agglomeration is conducted in a agglomeration drum, immediately prior to stacking of the heap. In the
20 agglomeration process the fine particles stick to the coarser particles and thereby make the subsequently formed heap more permeable to the leach process solution. The fines in the heap are immobilised during agglomeration and cannot then migrate and give rise to blinding of the heap, and/or channelling of leach solution, which may otherwise lead to long leach times and to incompletely
25 leached pockets within the heap.

The practice of acid agglomeration in the treatment of base metal oxide ores also has a benefit in "kick starting" the leaching process itself. The acid added during

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agglomeration contributes towards the total acid demand of the leach process and thereby improves the kinetics of the leach.

During acid agglomeration the acid is typically added to the agglomeration drum as concentrated sulphuric acid. Water or process solution may also be added to

- 5 the drum, usually at a time after addition of the acid. Agglomerated ore is typically stacked and left to cure for a period of up to several weeks. During the curing period, certain of the components of the ore that had been dissolved by the acid during the agglomeration process, re-precipitate and act to bind the ore together.
- 10 Having stacked the heap as described above, a network of irrigation pipes is laid over the heap. This allows a solution of sulphuric acid, at a suitable strength, to be applied to the heap to leach out the copper. The leach can take place over a period of a few months to several years. The pregnant leach solution reporting at the base of the heap may be recycled through the heap or sent for further treatment to recover the copper.
- 15

Conventionally, laterite ores and concentrates are subjected to either smelting, roasting or pressure acid leaching processing routes. The nature of laterite ores and concentrates have typically required processing options that are more aggressive than heap leaching.

- 20 It is now envisaged by the inventor and applicants that a heap leaching process similar to that described above may be applicable to the treatment of nickel and cobalt oxide ores, including laterite ores that are found in many locations around the world.

- Whilst there has been some discussion directed to the heap leaching of laterite
- 25 ores none appear to be commercialised. In a paper titled "Extraction of nickel and cobalt from Greek low-grade nickel oxide ores by heap leaching" (Canadian Institute of Mining, Sudbury, Canada XP002183410, pages 489 to 502) the authors, Agatzini-Leonardou, Dimaki and Boskos, describe a column leach (simulating a heap leach) of a low-grade nickel oxide ore with sulphuric acid at

ambient temperature. International Patent Application PCT/US01/10137 discloses a heap leach of nickel containing laterite ore, again utilising a sulphuric acid leach. What is apparent from these disclosures is that whilst nickel recoveries are reasonable, the recoveries of cobalt and other metals is
5 particularly poor.

The present invention has as one object thereof to overcome the abovementioned problems associated with the prior art or to provide a useful alternative thereto.

The preceding discussion of the background art is intended to facilitate an
10 understanding of the present invention only. It should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was part of the common general knowledge in Australia as at the priority date of the application.

Throughout the specification, unless the context requires otherwise, the word
15 "comprise" or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

Disclosure of the Invention

In accordance with the present invention there is provided a method for the heap
20 leaching of base metals from oxide ores, the method characterised by the method steps of:

- a) Establishing at least one heap of the oxide ore containing the base metals to be leached;

- b) Irrigating at least one of the or each heaps with a leach solution containing both sulphuric acid and dissolved sulphur dioxide; and
25

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- c) Providing at least one leach solution pond or other suitable container to which pregnant leach solution recovered at or near a base of the or each heap may be fed.

Preferably, a bleed of the pregnant leach solution from the or each heap may be

- 5 passed to a base metal recovery circuit.

Still preferably, the metal oxide ore is a laterite ore containing nickel and cobalt.

In one form of the invention, the ore may have been agglomerated with sulphuric acid prior to forming the or each heap.

- The sulphur dioxide is preferably provided in the form of either sodium
10 metabisulphite or burned elemental sulphur.

In one form of the invention sodium metabisulphite is added to a sulphuric acid leach solution prior to application to the or each heap.

- The sodium metabisulphite may be provided such that the resulting leach solution contains between about 1 to 40g/l thereof, and preferably about 5g/l
15 thereof.

Preferably, sodium metabisulphite is added regularly to the leach solution throughout the leach. The concentration of sodium metabisulphite in the leach solution is preferably maintained at or about 5g/l throughout the leach.

- In one form of the present invention sodium metabisulphite is added regularly to
20 the leach solution at intervals of about 2 weeks throughout the leach.

Preferably, the sulphuric acid leach solution is provided at a concentration of about 75g/l.

Brief Description of the Drawings

The present invention will now be described, by way of example only, with reference to one embodiment of the present invention and the accompanying drawings, in which:-

- 5 Figure 1 is a diagrammatic representation of a simple leach circuit exemplifying the method of the present invention;

Figure 2 is a graphical representation of the comparative nickel leach kinetics obtained with leach solutions containing either 10g/l sodium metabisulphite plus 75g/l sulphuric acid, or with only 75g/l sulphuric acid;

- 10 Figure 3 is graphical representation of the comparative cobalt leach kinetics obtained with leach solutions containing either 10g/l sodium metabisulphite plus 75g/l sulphuric acid, or with only 75g/l sulphuric acid;

Figure 4 is a graphical representation of nickel recovery in Bottle Rolls Tests 1 to 7;

- 15 Figure 5 is a graphical representation of cobalt recovery in Bottle Rolls Tests 1 to 7; and

Figure 6 is a graphical representation of iron recovery in Bottle Rolls Tests 1 to 7.

Best Mode(s) for Carrying Out the Invention

- 20 In Figure 1 there is shown a flow-sheet demonstrating one potential commercial application of a heap leach in accordance with the present invention. A heap 10 is stacked on an impermeable membrane 12 in known manner. Similarly, piping is provided to direct pregnant leach solution to a sump 14, from which the pregnant leach solution may flow by gravity to a leach solution pond 16, or may
25 be bled from the leaching process to a base metal recovery circuit.

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The heap 10 has arranged thereon a reticulation system 18 to feed the heap 10 with leach solution from the leach solution pond 16, via a pump 20. The sump 14 contains a pump (not shown).

The heap 10 is composed of laterite ore containing nickel and cobalt, the ore
5 having been crushed to a size of 100% passing 0.25 inches and agglomerated
with sulphuric acid prior to stacking.

The leach solution pond 16 is maintained at a suitable acid strength or pH by the
addition of sulphuric acid. As leach solution is pumped via pump 20 and
reticulation 18 to the ore heap 10, sulphur dioxide is introduced, whereby the
10 level of acid and sulphur dioxide in solution is raised to a level determined by the
user. The source of sulphur dioxide in the present example is sodium
metabisulphite (SMS), although it is envisaged by the inventor and applicant that
other sources of sulphur dioxide may be utilised, including burned elemental
sulphur, and may include any means of producing sulphur dioxide in either a
15 gaseous, liquid, or aqueous form.

In Figures 2 and 3 are shown graphical representations of comparative leach
kinetics for nickel and cobalt, respectively, when leached with either a
combination of 10g/l sodium metabisulphite and 75g/l sulphuric acid, or with 75g/l
sulphuric acid only, in a column leach simulation of a heap leach process.

20 As can be seen with reference to each of Figures 2 and 3, the use of a leach
solution containing sodium metabisulphite in addition to sulphuric acid results in
increased recoveries of both nickel and cobalt, with the most marked
improvement being found with respect to cobalt recovery. The improved base
metal recovery is evidenced almost immediately and remains throughout the
25 period of the experiment, to fifty days or over.

Whilst the examples where conducted with 10g/l sodium metabisulphite it is
envisaged that any level between about 1 to 40g/l sodium metabisulphite, or its
equivalent dosage of sulphur dioxide, will achieve the objects of the invention.
The inventor and applicant have also specifically found effectively identical

results with 5g/l sodium metabisulphite in combination with sulphuric acid as the leach solution.

The mechanism by which the SMS contributes to recovery of the metal values is largely uncertain, although the inventor and applicant believe that the SMS

- 5 contributes to the reduction of multivalent metals to their more soluble (and more reduced) species. For example, Co³⁺ may be reduced to Co²⁺, making it more soluble and consequently more readily leached.

It is also possible that the reduction of any MnO₂ present by the SMS, such that Mn⁴⁺ is reduced to the more soluble Mn²⁺, may destabilise the nickel and cobalt

- 10 present, making it in turn more readily leached, or more readily reduced and then leached.

In Figures 4 to 6 are shown the results of Bottle Rolls testing undertaken on a sample of nickel containing ore so as to investigate further the conditions applicable for the method of the present invention.

- 15 The bottle rolls tests were undertaken using 150g of sample and 1.5 litres of 75 g/l sulphuric acid solution. The varied conditions for the seven tests are given below:

- Test 1 - standard test with 5g/l SMS added when leaching stops.
- Test 2 - standard test with 5g/l SMS added at start.
- 20 • Test 3 - standard test with 10g/l SMS added when leaching stops.
- Test 4 - standard tests with 10 g/l SMS added at start.
- Test 5 - 20 g/l SMS added when leaching stops
- Test 6 - 40 g/l SMS added when leaching stops

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- Test 7 - staged addition, with 5g/l SMS added at beginning and repeatedly at two week intervals.

The tests were stopped after 266 days and recoveries of iron, nickel and cobalt are given in Table 1 and Figures 4, 5 and 6.

5

Table 1 – Bottle Rolls Leach recoveries on Bulk sample

Test	Recovery %		
	Fe	Ni	Co
1	39.9	76.0	95.2
2	39.1	75.2	94.8
3	47.6	79.1	94.5
4	44.1	77.7	94.4
5	47.0	79.5	93.9
6	48.7	79.4	79.5
7	53.6	82.6	93.8

Nickel recoveries ranged from 75.2% (Test 2) to 82.6% (Test 7). In general, it took approximately 35 days to recover 50% of the nickel but 160 days to recover 70% and 266 days to recover 75-80% of the nickel. Nickel recovery was still increasing marginally after 266 days. Maximum recovery was achieved in Test 7 where sodium metabisulphite (SMS) was added every 14 days.

Cobalt extraction was very rapid when SMS was added (Tests 2, 4 and 7) with cobalt recoveries of 90% after 14 days. Cobalt leaching was considerably slower when SMS was not added, typically with recoveries of 45-50% after 133 days.

15 Addition of SMS at this time (Tests 1, 3 and 5) rapidly increased recovery to around 90%.

Iron recovery ranged from 39.1% (Test 2) to 53.6% (Test 7). Again, iron recovery was highest when SMS was added throughout the test. Acid consumptions ranged from 195kg/t (Test 3) to 310 kg/t (Test 5).

20 Modifications and variations such as would be apparent to the skilled addressee are considered to fall within the scope of the present invention.

Claims

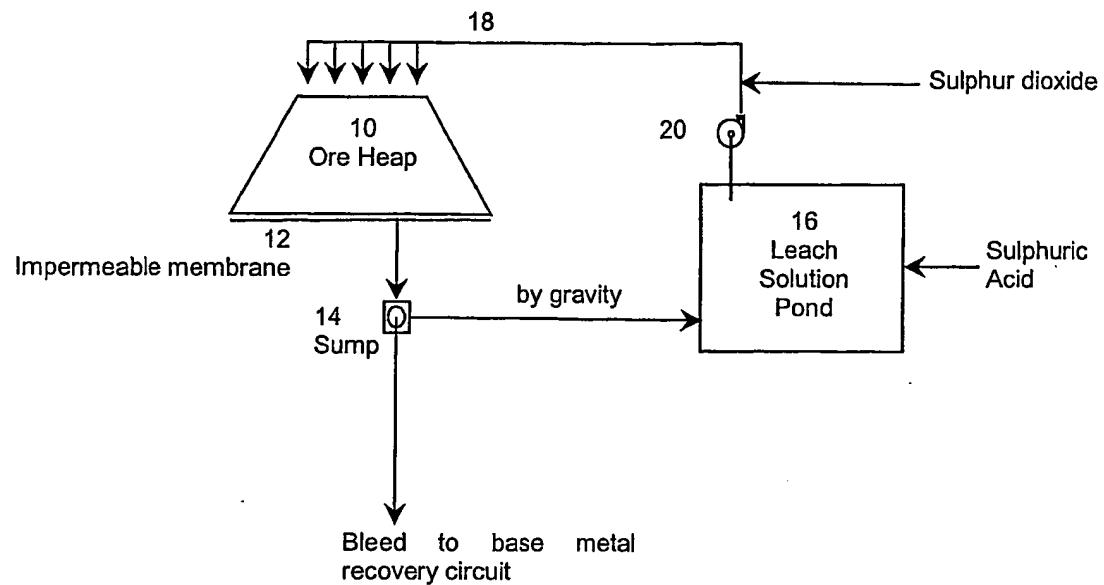
1. A method for the heap leaching of base metals from oxide ores, the method characterised by the method steps of:
 - a) Establishing at least one heap of the oxide ore containing the base metals to be leached;
 - b) Irrigating at least one of the or each heaps with a leach solution containing both sulphuric acid and dissolved sulphur dioxide; and
 - c) Providing at least one leach solution pond or other suitable container to which pregnant leach solution recovered at or near a base of the or each heap may be fed.
2. A method according to claim 1, characterised in that a bleed of the pregnant leach solution from the or each heap is passed to a base metal recovery circuit.
3. A method according to claim 1 or 2, characterised in that the metal oxide ore is a laterite ore containing nickel and cobalt.
4. A method according to any one of the preceding claims, characterised in that the ore is agglomerated with sulphuric acid prior to forming the or each heap.
5. A method according to any one of the preceding claims, characterised in that the sulphur dioxide is provided in the form of either sodium metabisulphite or burned elemental sulphur.
6. A method according to claim 5, characterised in that sodium metabisulphite is added to a sulphuric acid leach solution prior to application to the or each heap.

- 10 -

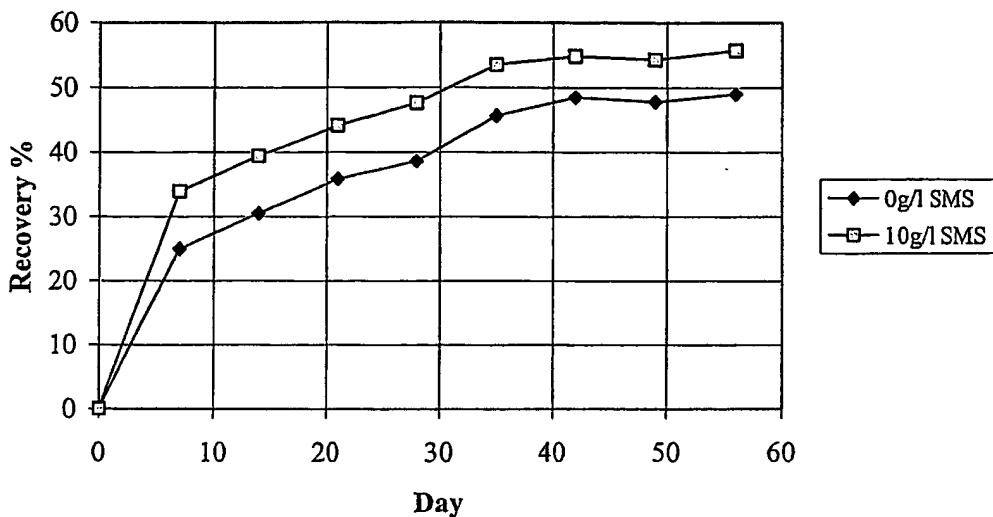
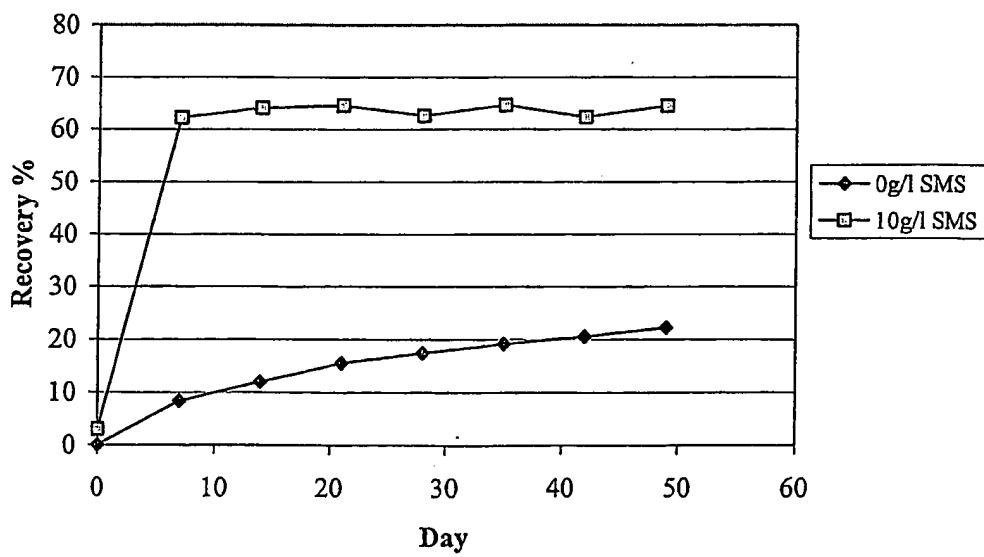
7. A method according to claim 5 or 6, characterised in that the sodium metabisulphite is provided such that the resulting leach solution contains between about 1 to 40g/l thereof.
8. A method according to claim 7, characterised in that the sodium metabisulphite is provided such that the resulting leach solution contains about 5g/l thereof.
5
9. A method according to any one of claims 5 to 8, characterised in that sodium metabisulphite is added regularly to the leach solution throughout the leach.
10. A method according to claim 9, characterised in that the concentration of sodium metabisulphite in the leach solution is maintained at or about 5g/l throughout the leach.
10
11. A method according to claim 9 or 10, characterised in that sodium metabisulphite is added regularly to the leach solution at intervals of about 2 weeks throughout the leach.
- 15 12. A method according to any one of the preceding claims, characterised in that the sulphuric acid leach solution is provided at a concentration of about 75g/l.
13. A method substantially as hereinbefore described with reference to the accompanying figures.

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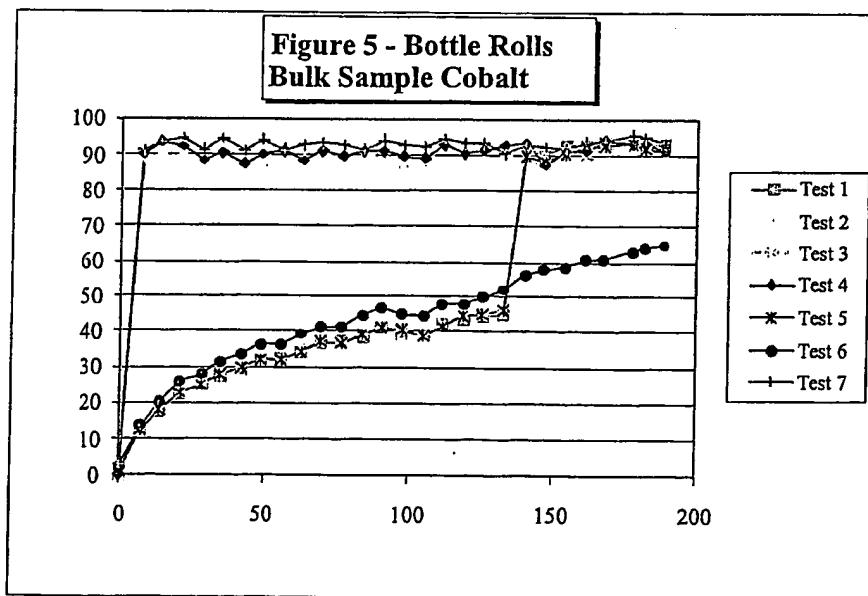
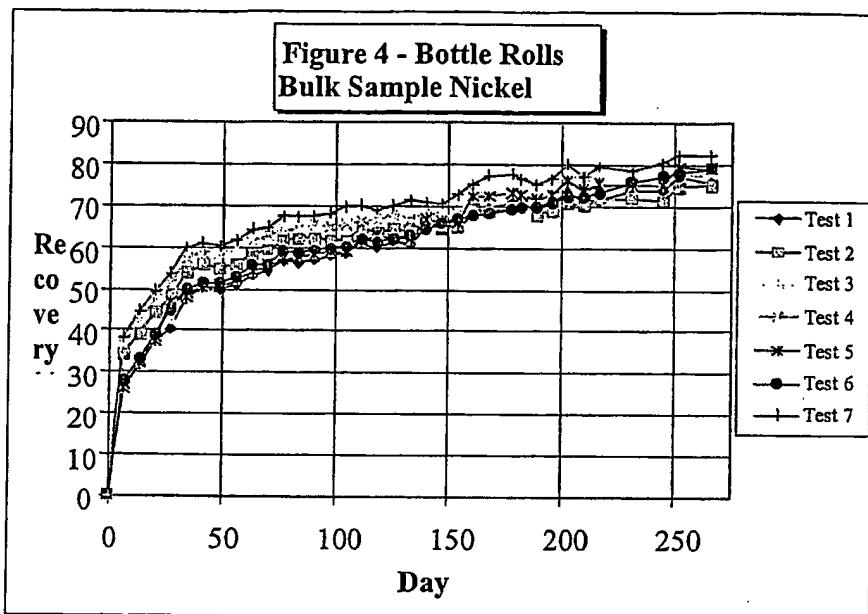
Figure 1



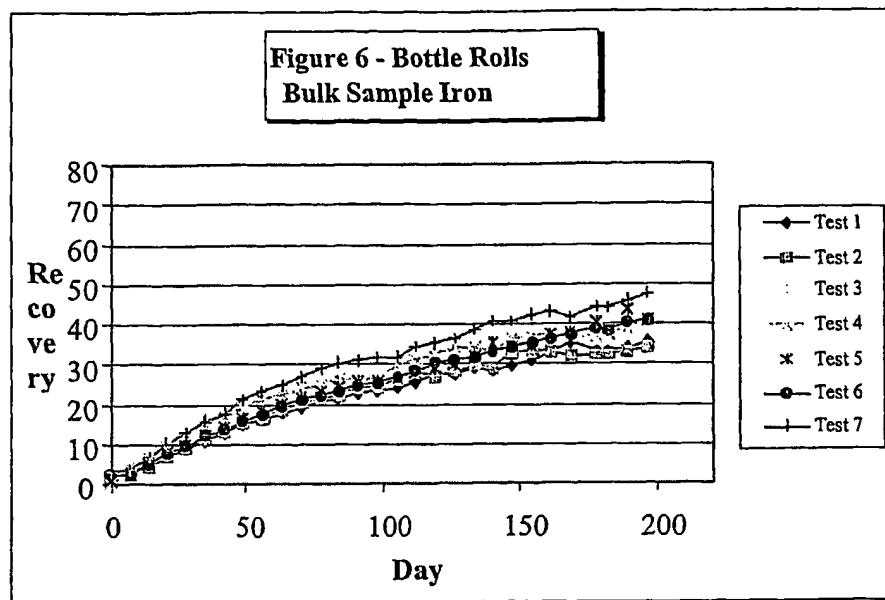
2/4

Figure 2 - Nickel Recovery**Figure 3 - Cobalt Recovery**

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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB 03/04252

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22B3/08 C22B23/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 320 665 A (MULLINS KIERAN) 14 June 1994 (1994-06-14) example 3; col.4, line 57 - col.5, line 3 ---	1, 5-7
Y	WO 00 48944 A (MBX SYSTEMS INC) 24 August 2000 (2000-08-24) claims 41, 43, 44, 47, 48, 51, 55; page 13, lines 6-12 ---	1-7, 9, 11, 12
Y	WO 01 75184 A (BHP MINERALS INT INC) 11 October 2001 (2001-10-11) cited in the application claims ---	1-7, 9, 11, 12

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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19/01/2004

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 03/04252

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	YOUZBASHI A A ET AL: "LEACHING OF CU2O WITH AQUEOUS SOLUTION OF SULFUR DIOXIDE" METALLURGICAL TRANSACTIONS B. PROCESS METALLURGY, METALLURGICAL SOCIETY OF AIME. NEW YORK, US, vol. 24B, no. 4, 1 August 1993 (1993-08-01), pages 563-570, XP000387542 page 563, right column, lines 5-14 -----	1-13
A	WO 96 41025 A (PACIFIC NICKEL CORP) 19 December 1996 (1996-12-19) -----	

INTERNATIONAL SEARCH REPORT

Internati	plication No
PCT/GB	03/04252

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5320665	A 14-06-1994	IE AU AU CA ZA	912171 A1 657139 B2 1850192 A 2072188 A1 9204606 A	30-12-1992 02-03-1995 07-01-1993 25-12-1992 31-03-1993
WO 0048944	A 24-08-2000	AU BR CA TW WO US US ZA	3370500 A 0008962 A 2363031 A1 528732 B 0048944 A1 2003075021 A1 6471743 B1 200106808 A	04-09-2000 27-11-2001 24-08-2000 21-04-2003 24-08-2000 24-04-2003 29-10-2002 21-08-2002
WO 0175184	A 11-10-2001	US AU BR CA EP JP WO ZA	6312500 B1 5520401 A 0109795 A 2404003 A1 1272680 A2 2003529679 T 0175184 A2 200207784 A	06-11-2001 15-10-2001 21-01-2003 11-10-2001 08-01-2003 07-10-2003 11-10-2001 11-04-2003
WO 9641025	A 19-12-1996	AU WO	5888896 A 9641025 A1	30-12-1996 19-12-1996